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Elemental and organic carbon in the urban environment of Athens. Seasonal and diurnal variations and estimates of secondary organic carbon

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ABSTRACT

Elemental and organic carbon (EC and OC) hourly concentrations were measured continuously, at an urban location in central Athens, Greece, for an 8-month period (January–August). Average concentrations of 2.2 μgC m^{-3} and 6.8 μgC m^{-3} were observed, for EC and OC, respectively. The combined contribution of carbonaceous compounds (EC plus organic matter) to PM_{10} was calculated at 26%. The seasonal variability of EC was limited, while OC mean concentrations were significantly higher (by 23%), during the warm months (May–August). The weekly variation followed a different pattern, with the weekend decrease of EC levels (25%) being more pronounced than of OC (14%). EC produced a bimodal diurnal cycle, with the morning rush hour traffic mode prevailing. The OC mean circadian variation displayed those peaks as well. However, midday-to-afternoon presence of secondary organic aerosol (SOA) was strongly indicated. The conditional probability function was used to assess the impact of wind direction. High EC, OC levels were linked to southern flows, which during summer are mainly related to the appearance of sea breeze circulation. The temporal variation of EC, OC and their correlation patterns with primary and secondary gaseous pollutants, suggested that, although primary emissions affected both fractions, SOA formation is an important factor to be accounted for, especially during the photochemical season. Secondary organic carbon was estimated using the EC tracer method and orthogonal regression on OC, EC hourly concentration data. The average contributions of secondary organic carbon (SOC) to OC were calculated at 20.9% for the cold period and 30.3% for the warm period. Maximum values of 58% and 91% were estimated for daily and hourly contributions, respectively. The SOC diurnal variations suggested photochemical formation throughout the year, intensified during summer months, with the correlation coefficient between SOC and the sum of oxidants ($NO_2 + O_3$) reaching up to 0.84.

1. Introduction

Elemental and organic carbon fractions constitute a major portion of atmospheric particles. At European urban areas, their combined contribution is known to reach up to 25–40% of PM_{10} and 30–50% of $PM_{2.5}$ (Putaud et al., 2004). Recent epidemiologic studies, benefiting on the increasing availability of long PM chemical composition time-series, have demonstrated the risks of exposure to increased levels of urban carbonaceous aerosols, revealing notable associations with cardiovascular mortality and morbidity (Ostro et al., 2007; Ito et al., 2011). Moreover, the OC mixture includes compounds like PAHs and PCBs, known for their potential to induce carcinogenic and mutagenic effects (WHO, 2000).

Existence of long-term and high-time resolution EC–OC data is important in order to explore their dynamics, resolve their sources and effectively implement mitigation strategies. EC is a primary species produced by incomplete combustion. In contrast, OC anthropogenic or biogenic, can be emitted directly into the air (primary organic carbon, POC) or formed in the atmosphere through reactions of organic precursors with oxidative species and subsequent gas-to-particle partitioning of the less volatile products (secondary organic carbon, SOC). Contributions of primary and secondary organic aerosol components are difficult to directly quantify by chemical analysis, because OC is a complex mixture of hundreds of compounds, with a variety of chemical and physical properties. Researchers have employed several indirect methods to estimate the amount of primary and secondary organic aerosol. The EC tracer method (Turpin and Huntzicker, 1991; Turpin and Huntzicker, 1995) has found the widest application, due to its simplicity and reliance on ambient EC, OC measurements alone (Castro et al., 1999; Lim and Turpin, 2002; Cabada et al., 2004; Polidori et al., 2006; Harrison and Yin, 2008; Pio et al., 2011).

The area of Athens can be seen as particularly challenging for the study of primary and secondary carbonaceous aerosols. The Athens basin (450 km^2) has over 4 million inhabitants. Emissions from the road transport sector are dominant, with the number of vehicles in

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circulation exceeding 2 million. The topography of the area (Fig. 1) is rather unfavorable for dispersion of air pollutants, with the basin being surrounded by mountains, on three sides. Particulate matter is considered as the highest priority pollutant, with elevated concentrations consistently recorded across the area (Chaloulakou et al., 2005; Grivas et al., 2008a; Theodosi et al., 2011). The prevailing Mediterranean climate type is characterized by hot dry summers, mild winters and a high frequency of cloudless, sunny days, throughout the year (Kassomenos et al., 1995). Irradiance is very intense – especially during the warm season – and promotes the formation of photo-oxidation products. As a result, severe levels of O_3 are frequently observed.

It appears that primary and secondary components of carbonaceous aerosol should be systematically studied. However, until now this has been done only occasionally. Sillanpaa et al. (2006) measured EC and OC in central Athens for 7 weeks in the summer, with a time resolution of 3–4 days. In other areas of Greece, Terzi et al. (2010) have reported EC and OC levels from Thessaloniki, while Koulouri et al. (2008) provided data on the regional background of Southern Greece.

To our knowledge, this is the first time in Athens that a study aims to:

- provide a reference base of long-term EC and OC measurements, at a site representative of pollution characteristics at urban locations.
- examine the variations of their concentrations at a seasonal, weekly and diurnal level and gain insights on sources, formation/transport processes and effects of meteorological conditions.
- apply and parameterize the EC tracer method, in order to obtain realistic estimates of secondary organic carbon, on a high temporal resolution, exploring its variations and the factors which control them.

2. Methodology

2.1. Study area

The study period covered the months January to August 2003. Measurements were performed at a monitoring station of the National Air Pollution Monitoring Network, at the eastern part of central Athens (Fig. 1). A total of 189 days with concurrent EC and OC measurement were included in the present study. The sampling location (Goudi-GOU) experiences moderate traffic conditions. Sampling was conducted at a height of 4 m. The distance from the nearest road was 10 m, where the traffic density was estimated at 14,000 motor vehicles per day. A larger road, with an estimated traffic volume of more than 40,000 motor vehicles per day, crosses at a distance of 30 m from the station. The vehicle population profile in these roads, included diesel powered vehicles (heavy duty diesel vehicles-HDDV, taxies and buses) at a percentage of approximately 6%. Diesel oil was almost exclusively used as fuel for domestic heating in the area. Three large hospitals are located in close vicinity to the site. Thus, measured concentration levels are important for the exposure of sensitive population subgroups.

Fig. 1. Overview of the Athens basin. EC and OC measurements conducted at GOU (●). Additional air quality (■) and weather stations (○) also displayed.

2.2. OC–EC and PM_{10} monitoring

An ambient carbon particulate monitor (ACPM 5400, Rupprecht and Patashnik Co. Inc.) was used for continuous (hourly) concentration measurements of EC and OC. The instrument utilizes a CO_2 infrared detector, to measure CO_2, released from oxidized carbonaceous particles, previously collected on an impactor. The separation of organic and elemental carbon fractions is achieved by thermal differentiation. The temperature of 340 °C was used as the dividing point (Holler et al., 2002). The organic component is defined as the material which is volatilized up to this temperature and the remaining fraction is elemental carbon, extracted from the collector by heating up to 750 °C. The instrument was regularly calibrated using zero grade air and high purity span gas (CO_2). Ambient air was pumped at a rate of 16.7 l min^{-1}, through a PM_{10} inlet.

The precision of the method, as characterized by measurements of collocated ACPM monitors, is reported to be high (Even et al., 1998; Cowen et al., 2001), with correlations (r) exceeding 0.95 and low coefficients of variability. The main uncertainty associated with the operation of the ACPM5400 is the underestimation of EC in the ultrafine particle region, due to the collection of particle mass on an impactor, with a 50% cut-off diameter at 0.14 μm. EC exhibits bimodality in urban aerosols and a substantial portion is expected to be in the <0.1 μm range, when only a small fraction of OC is expected below 0.2 μm (McMurry and Zhang, 1989). Initial research indicated the possibility for important underestimations of EC concentrations, up to 40–60% (Even et al., 2000; Holler et al., 2002). Direct comparison with EC determined by thermal–optical methods has showed better agreement, at cases, with underestimations in the range of 17–26% (Lim et al., 2003; Venkatachari et al., 2006; Plaza et al., 2011). The magnitude of the negative artifact is dependent on local EC particle size distributions. Thus, a correction factor, applied to ACPM concentrations, should not only be site-specific, but also time-specific (Cowen et al., 2001). For example, on occasions, overestimation of EC concentrations by the ACPM has been reported, as well (Chow et al., 2006). In the absence of an inter-comparison, conducted at the conditions of the study location, it was decided that a correction factor for EC would not be used.

In order to investigate whether the ACPM adequately captured the variability of EC (the principal light absorbing species in the atmosphere), a separate experiment was conducted. The carbon monitor was operated for 25 days, while PTFE filters were concurrently sampled with a PM_{10} Harvard Impactor (Air Diagnostics Inc.), at 10 l min^{-1}. The reflectance of filters was measured with a smoke stain reflectometer (EEL43D, Diffusion Systems Ltd.) and the absorption coefficient (m^{-1}), was calculated, as a surrogate of black carbon content (ISO9835, 1993). The correlation coefficient between EC and the absorption coefficient was $r = 0.93$, revealing a very good agreement and being comparable to values reported for intercomparisons between the ACPM and optical methods (Even et al., 2000; Castanho and Artaxo, 2001). Several studies have explored associations between absorption coefficients calculated by reflectometry and EC determined by thermal–optical analysis (Kinney et al., 2000; Jannsen et al., 2001). Reported linear associations were ubiquitously well defined, with correlation coefficients in the range of